
Phase Transformations

Sections 8.4-8.6, 8th Ed.; Sections 6.1-6.3, 7th Ed.

Temperature-Composition Diagrams

- Distillation of Mixtures

- Azeotropes

- Immiscible Liquids

Liquid-Liquid Phase Diagrams

- Phase Separations

- Critical Solution Temperatures

- Distillation of Partially Miscible Liquids

Liquid-Solid Phase Diagrams

- Eutectics

- Reacting Systems

- Incongruent Melting

Last updated: Dec. 7, 2009, minor changes, added slides 18, 19 and 22, mod. 23

Temperature Composition Diagrams

Temperature composition diagrams show the boundaries of compositions of phases at equilibrium at different temperatures at a given pressure (typically 1 atm) - liquid phase in lower part of diagram

Region between lines: $F' = 1$, compositions of phases are fixed at given temperature

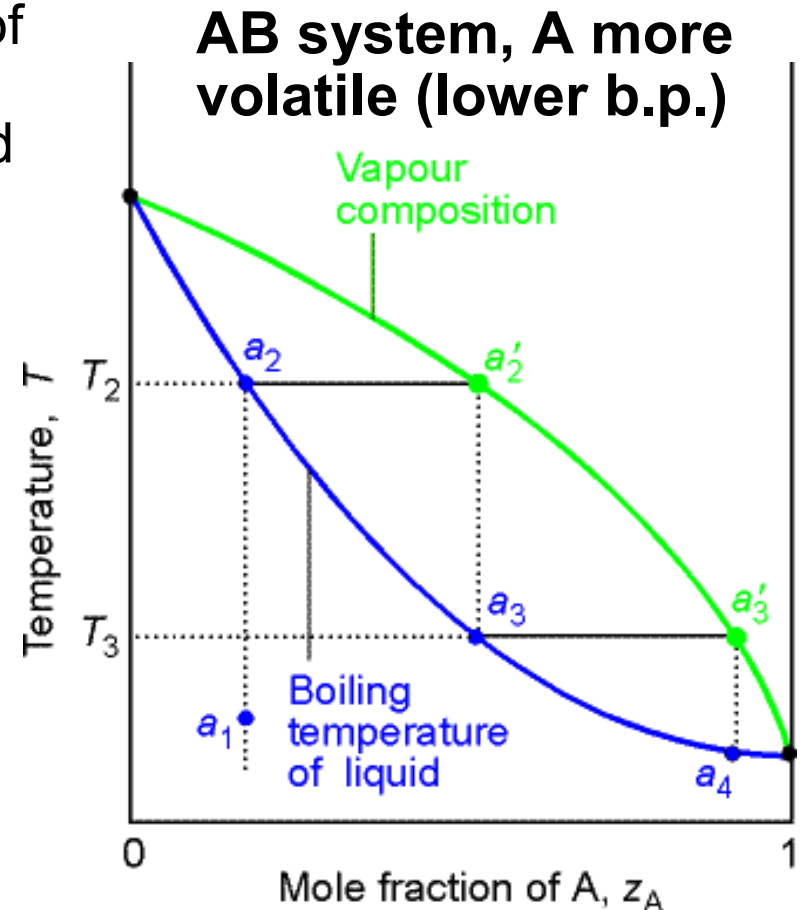
Region outside lines, $F' = 2$, temperature and phase composition are variable

a_1 : pure phase liquid is heated and boils at T_2 , with composition $a_2 = a_1$, vapour has minuscule component a_2' (location of the tie line gives us the b.p. T_2)

a_3 : first bit of condensation drawn off from a distillation (collect a_2'), richer in the more volatile component, with composition a_3'

a_4 : Vapour is drawn off, liquid condenses to this composition, very rich in volatile component, and almost pure A is obtained

Boiling and condensation cycle is known as **fractional distillation**



Fractional Distillation

Fractional distillation is similar to simple distillation except that a fractionating column is placed between the boiling flask and the condenser. The fractionating column is usually filled with glass or plastic beads, which improve the separation between the liquids being distilled.

- The glass beads in the fractionating column provide "theoretical plates" (i.e., additional surface area) on which the vapour can condense, re-evaporate, and condense again, essentially distilling the compound over and over.
- Hence, more volatile liquids approach the top of the column, and the less volatile liquids stay in the bottom.
- The more theoretical plates that are used, the higher the surface area, and the longer the distillation will take, and more energy is required to complete the distillation.

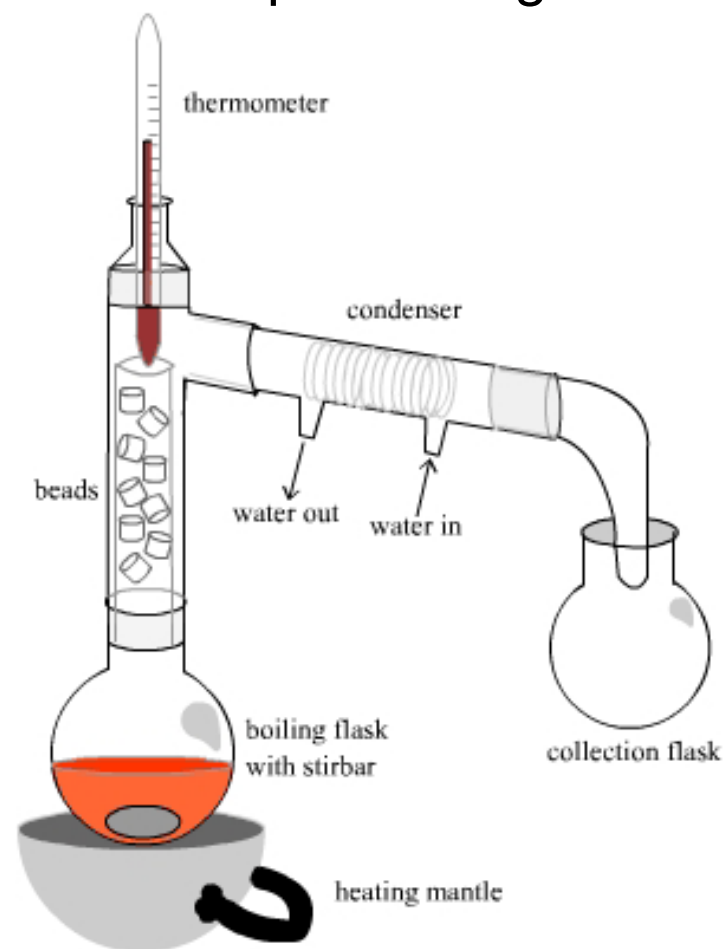
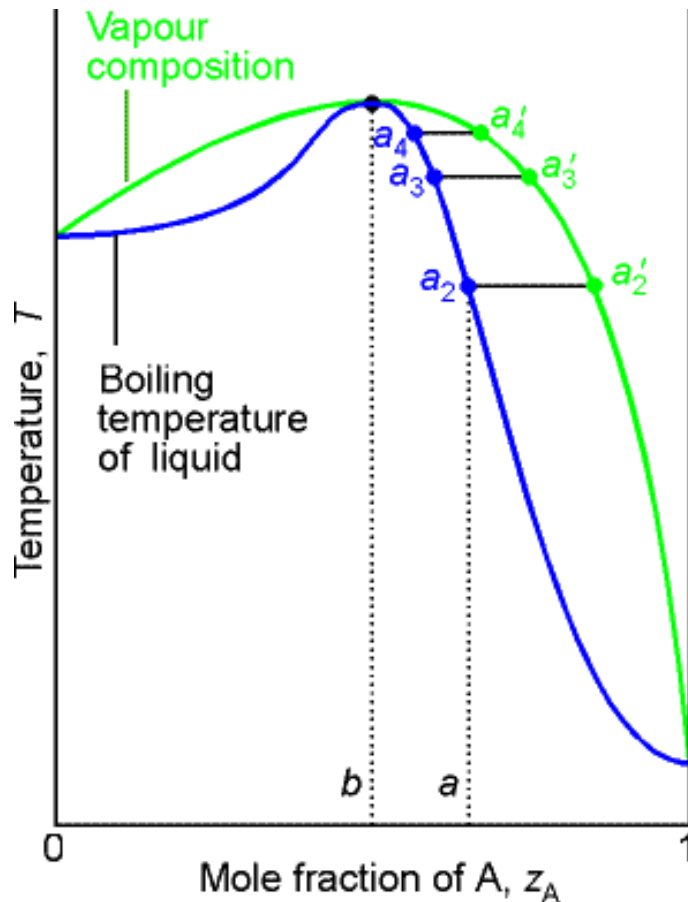


Image from: <http://www.chemhelper.com/distillation.html>

High-Boiling Azeotropes

Sometimes favourable interactions between molecules reduce vapour pressure of the mixture below the ideal value: i.e., A-B interactions stabilize the liquid phase - here $G^E = -ve$, more favourable for mixing

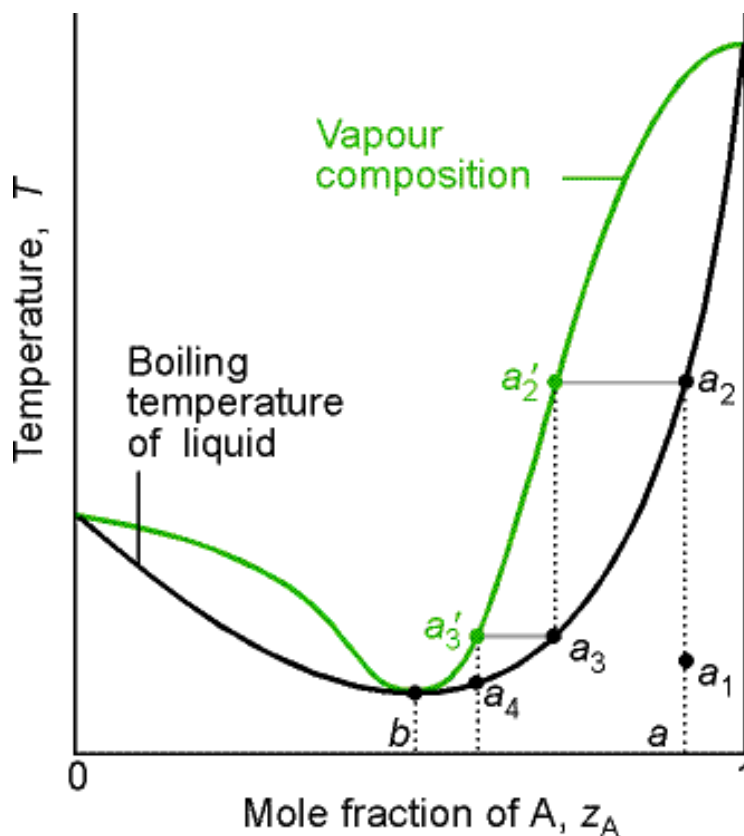


Examples: propanone/ trichloromethane and nitric acid/water mixtures

- **Composition a** heated to boiling ($a_2' > a_2$)
- Vapour (rich in A) is removed, and liquid left is richer in B, composition a_3 , vapour with a_3'
- Vapour removed, composition shifts to a_4 , vapour composition at a_4'
- Composition of remaining liquid shifts to b as more A is drawn off, and b.p. of liquid, vapour becomes richer in B
- Finally, at **composition b** the vapour of A has the same composition as the liquid
- Evaporation occurs without change in composition, and the mixture is an **azeotrope** (**boiling without changing**), & distillation cannot separate the components

Low-Boiling Azeotropes

The diagram below also shows azeotropic behaviour, except that the mixture is destabilized relative to the ideal solution (A-B interactions are unfavourable, G^E is +ve, less favourable to mixing)

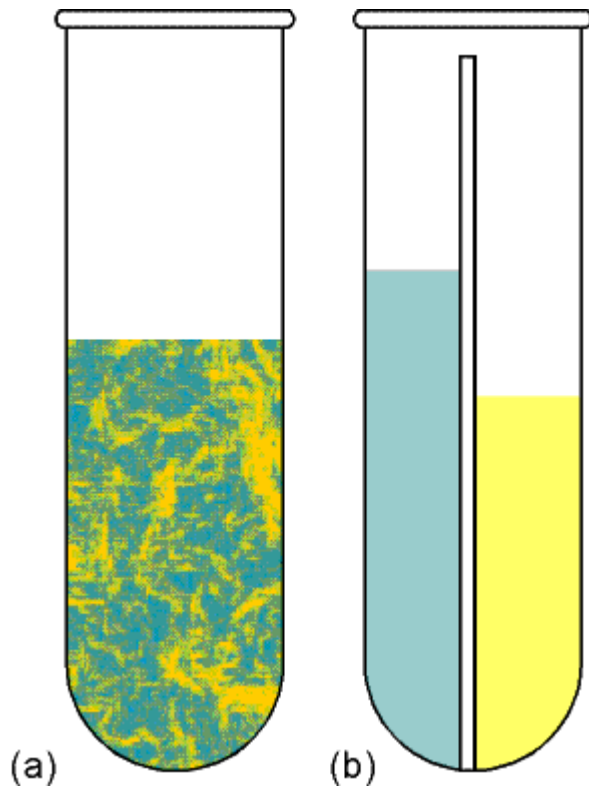


Examples: dioxane/ H_2O & ethanol/ H_2O

- Start at a_1 , boil at point a_2 , with vapour composition a_2'
- Vapour condenses to a_3 , vapour at a_3' composition, condensing higher up the fractional condensation tube to give composition a_4
- Azeotropic vapour comes out of the column at b , but not beyond

Immiscible Liquids

Distillation of two immiscible liquids A and B (example, octane and water) and at equilibrium, there is a tiny amount of A dissolved in B, and a tiny amount of B dissolved in A - liquids are saturated with the other component (in figure a)



The total vapour pressure is close to

$$p = p_A^* + p_B^*$$

If p = atmospheric pressure, then boiling commences, and the dissolved substances are purged from solution

Mixture is agitated, each component is kept saturated in the other component, purging continues until very dilute solutions are replenished

Mixing is essential, as separated components (figure b) would not boil at the same temperature

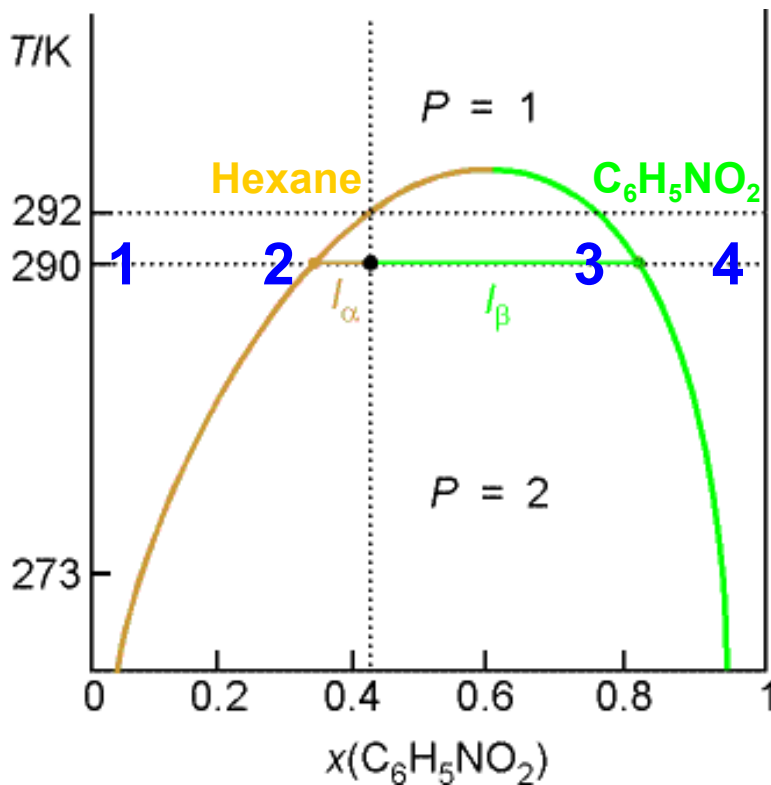
Presence of saturated solution means that components boil at a lower temperature than they would alone - basis of **steam distillation**

Liquid-Liquid Phase Diagrams

Partially miscible liquids are liquids that do not mix in all proportions at all temperatures

When $P = 2$, $F' = 1$ (prime denotes constant pressure), the selection of temperature makes the compositions of the immiscible phases fixed

When $P = 1$, $F' = 2$ (two liquids are fully mixed) both temperature and composition can be changed



- 1 Add small amt. of B to A at 290 K, it dissolves completely, single phase, $P=1$
- 2 Add more B to the point where B no longer dissolves, $P = 2$, major phase is A saturated with B, minor phase is B saturated with A (relative abundances are given by the **lever rule**)
- 3 Add enough B to dissolve all of the A, and system has single phase, $P=1$
- 4 Addition of more B dilutes the solution

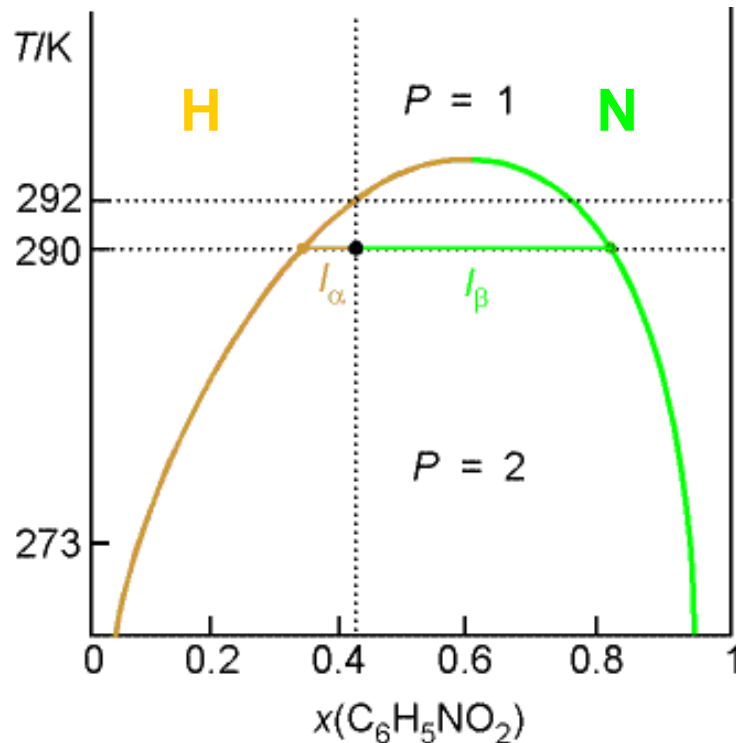
Compositions of two phases vary with changing temperature

Hexane and Nitrobenzene

Mixture of 50 g hexane (0.59 mol C_6H_{14}) and 50 g nitrobenzene (0.41 mol $\text{C}_6\text{H}_5\text{NO}_2$) was prepared at 290 K.

What are the compositions of the phases? To what temperature must the sample be heated to obtain a single phase?

At 290 K, point $x_N = 0.41$ occurs in a two phase region of the diagram, with the tie line cutting the boundary at $x_N = 0.35$ and $x_N = 0.83$ (these are the compositions of the two phases)



Ratio of amount of each phase:

$$\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha} = \frac{0.83-0.41}{0.41-0.35} = \frac{0.42}{0.06} = 7$$

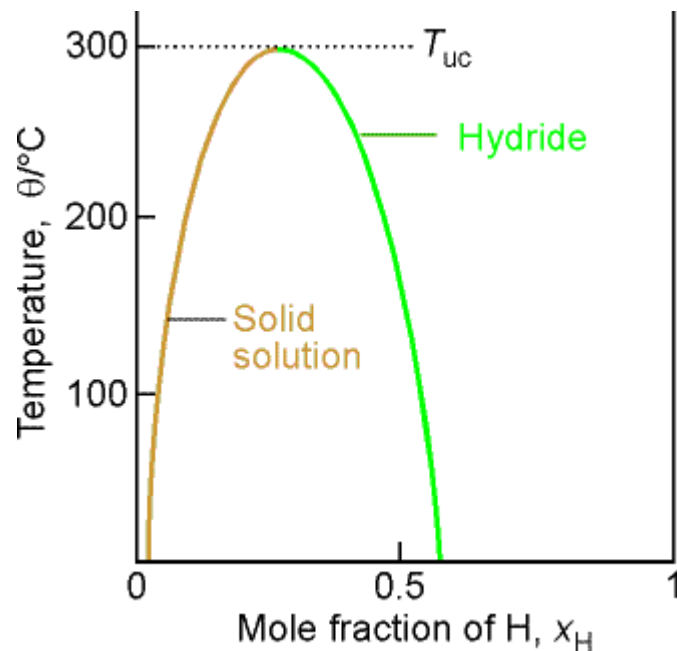
There is 7 times as much **hexane-rich phase** as there **nitrobenzene-rich** phase.

If the sample is heated to 292 K, we go into a single phase region

Critical Solution Temperatures

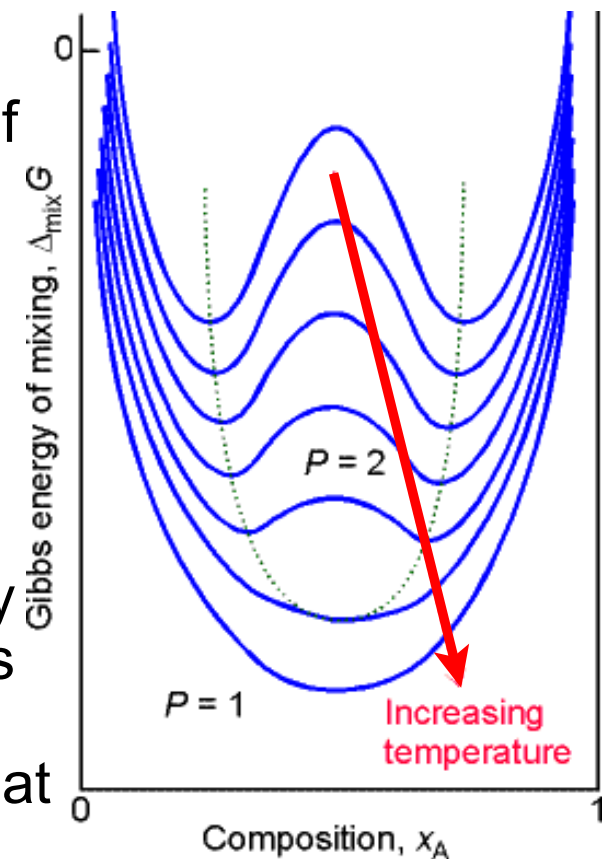
The **upper critical solution temperature**, T_{uc} , is the highest temperature at which phase separation occurs

This temperature exists since the thermal motion finally overcomes the potential energy advantage of certain molecules being close together



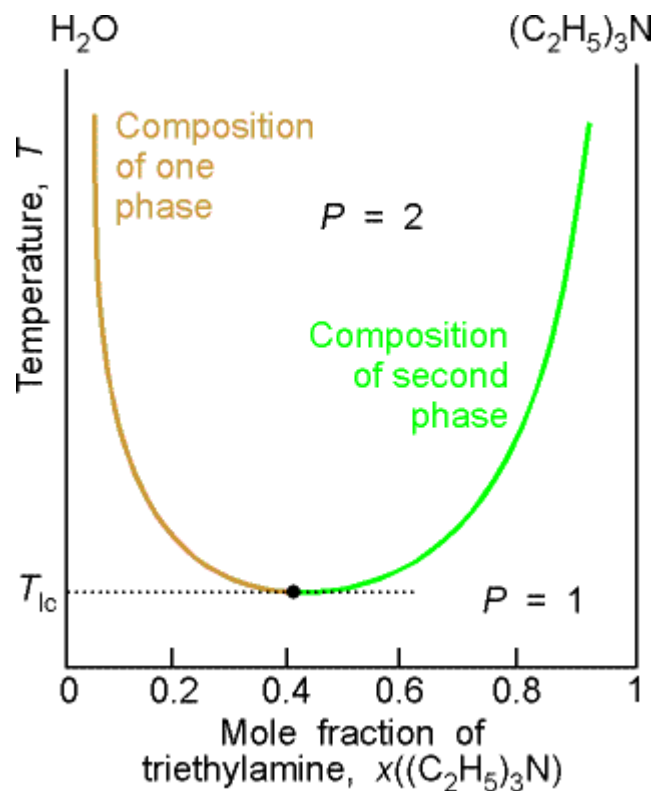
The Pd/H solid solution system has a solution of H_2 in Pd and palladium hydride up to 300°C , single phase at higher temperatures

Gibbs energy of mixing varies with T - double minima indicate partially miscible phases, and as the temperature rises, single minimum occurs at the upper critical temperature



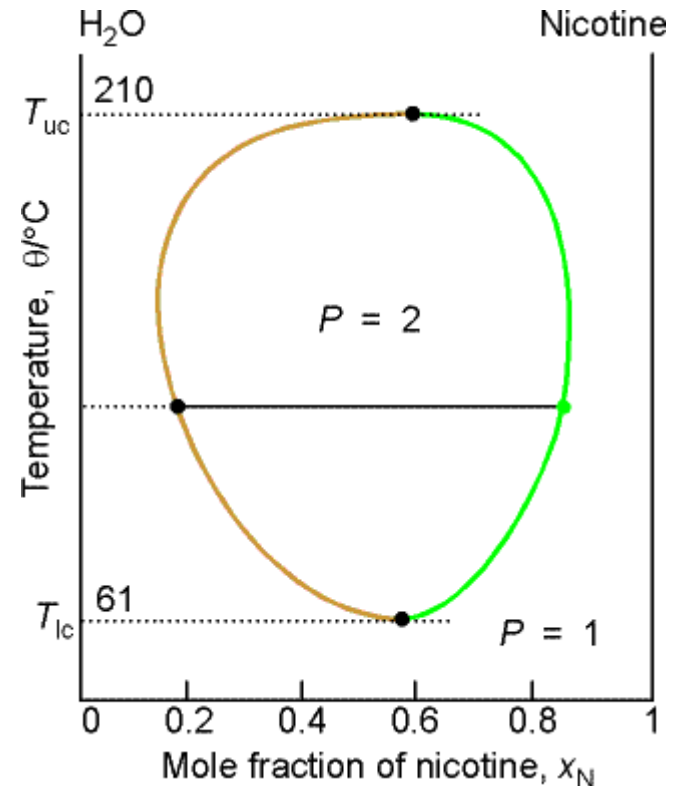
Critical Solution Temperatures, 2

The **lower critical solution temperature**, T_{lc} , is the lowest temperature at which phase separation occurs



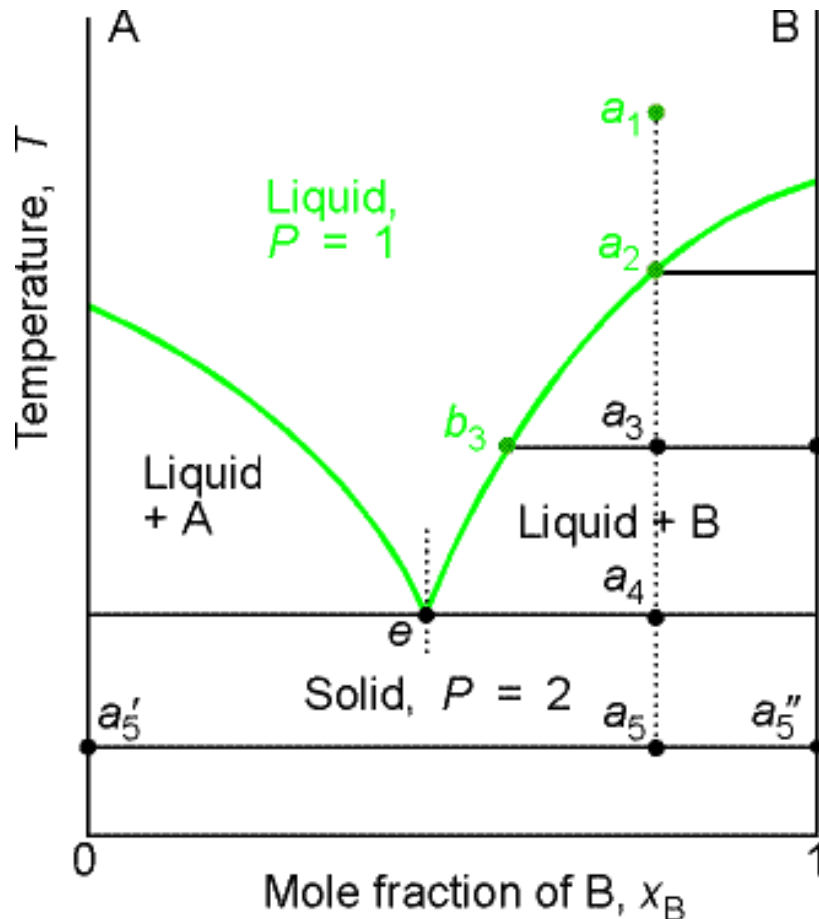
For triethylamine and water, the system is partially miscible above T_{lc} , and single phase below

Some systems have both T_{uc} and T_{lc} , with a famous example being nicotine in water, where $T_{uc} = 210^\circ\text{C}$ and $T_{lc} = 61^\circ\text{C}$



Liquid-Solid Phase Diagrams

Solid and liquid phases can be present below the boiling point (e.g., immiscible pair of metals right up to their melting points (As and Bi))



2-component liquid at temperature a_1 :

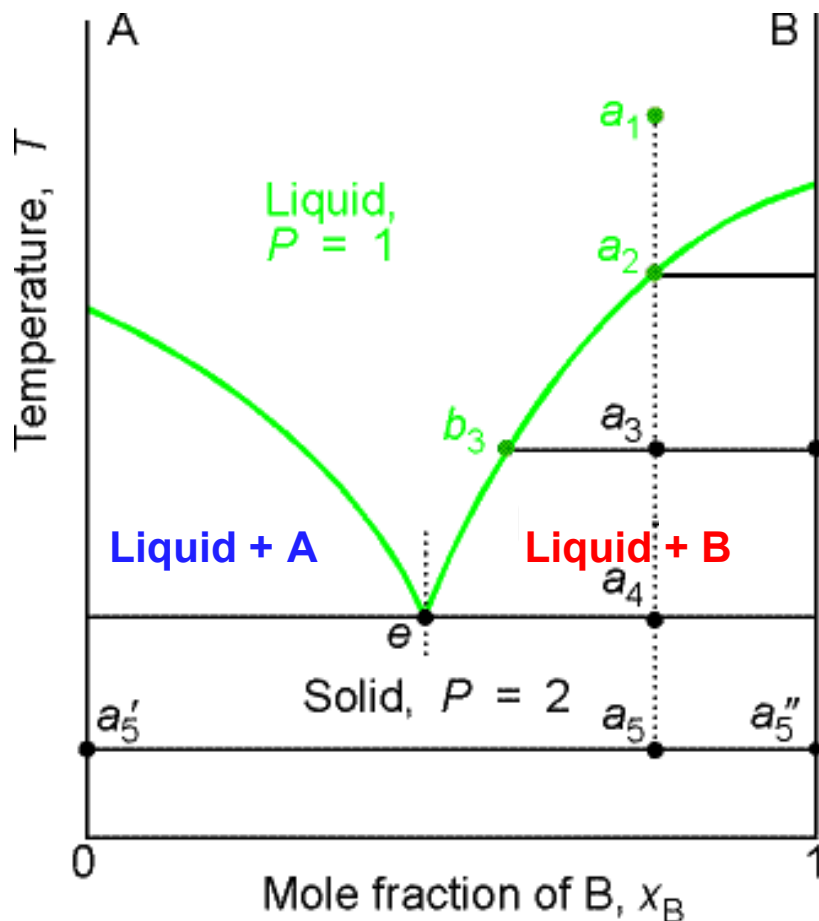
- (1) $a_1 \rightarrow a_2$ System enters "Liquid+B" pure solid B comes out of solution, remaining liquid richer in A
- (2) $a_2 \rightarrow a_3$ More solid B forms, equal amounts from lever rule, liquid even richer in A
- (3) $a_3 \rightarrow a_4$ Less liquid than at a_3 , composition given by e, liquid now freezes into a two component system of A and B

Composition at e is known as the **eutectic composition** (*easily melted*), and the horizontal line at e is known as T_e , the **eutectic temperature**.

Eutectics

Liquid with **eutectic composition** freezes at a single temperature, T_e , without depositing A or B in advance of the freezing point

Solid with eutectic composition melts, without any composition change, at the lowest temperature of any mixture



Compositions to the **left of e: deposit A as they cool - hypoeutectic**

Compositions to the **right of e: deposit B as they cool - hypereutectic.**

Only the eutectic solidifies at a single temperature ($F' = 0$ when $C = 2$ and $P = 3$), no other components unloaded

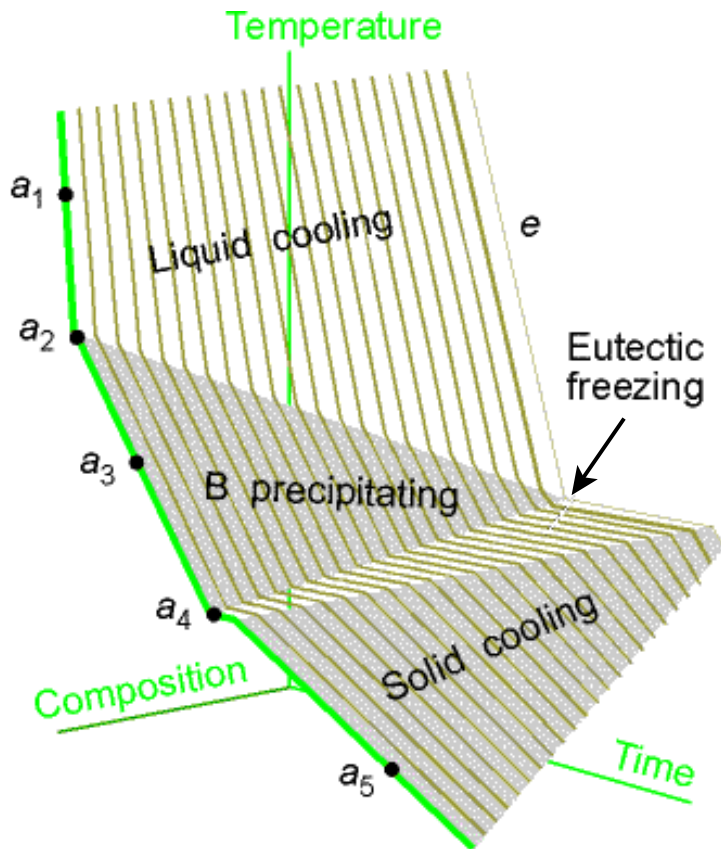
Examples:

- **Solder**, 67% tin and 33% lead, m.p. 183°C
- **23% NaCl, 77% H_2O** m.p. -21.1°C ; salt added to ice on a road (isothermal) mixture melts at $T > -21.1^\circ\text{C}$

Eutectic formation and thermal analysis

Eutectic formation happens in many binary alloy systems, important in alloy microstructure - eutectic solids have two phases, but crystallize in a homogeneous mixture of microcrystals (microscopy, X-rays, NMR)

Thermal analysis useful for detecting eutectics (this is done in the engineering department at the University of Windsor)



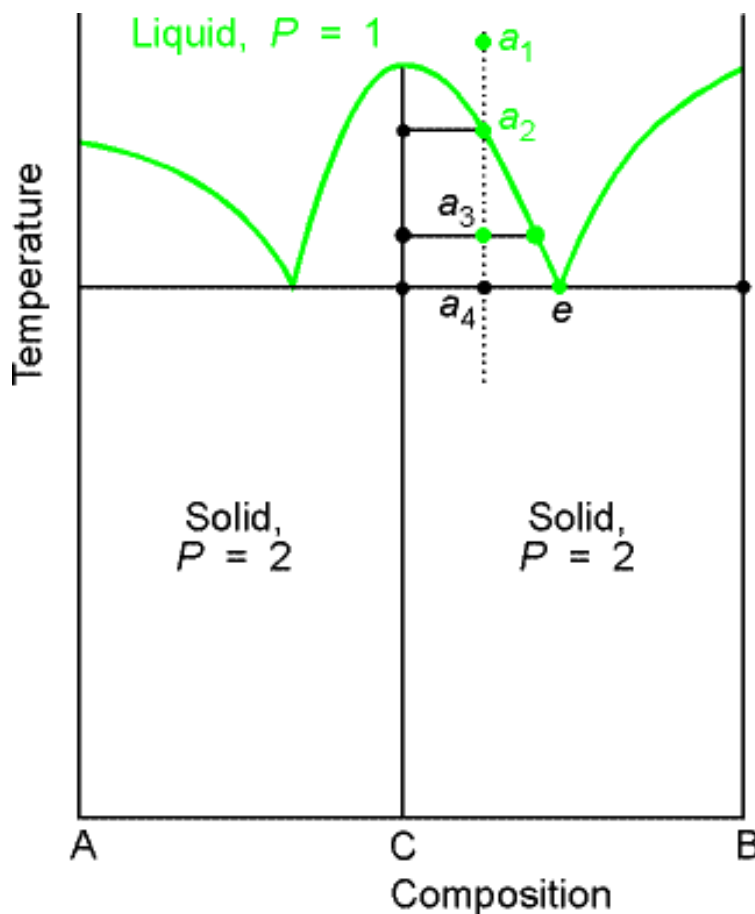
This type of analysis is conducted by cooling down an isopleth like the “a” isopleth from liquid to complete solid.

The place where the temperature remains constant over time is the **eutectic halt**

The **cooling curves** assist in making a phase diagram of the material for various temperatures and compositions.

Reacting Systems

Many binary systems react to produce different compounds - one important example is the formation of GaAs (gallium arsenide) which is very important for the **manufacturing of III/V semiconductors**:



System prepared with A (i.e., Ga) and excess of B (i.e., As) consists of C (i.e., GaAs) and unreacted B (i.e., As).

The binary B,C system forms a eutectic

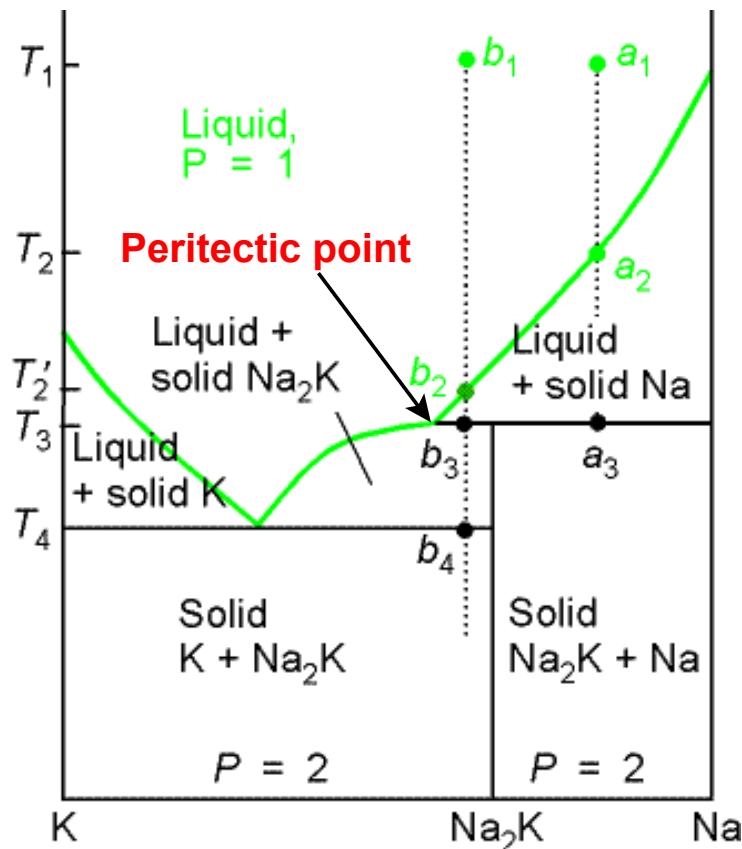
The important part of the phase diagram are the compositions of equal amounts of A and B ($x = 0.5$), pure A and pure B

Solid deposited along the cooling isopleth "a" is compound C

Below a_4 there are two solid phases, with some C and some B

Incongruent Melting

Sometimes component C is not stable as a liquid (e.g., alloy Na_2K)

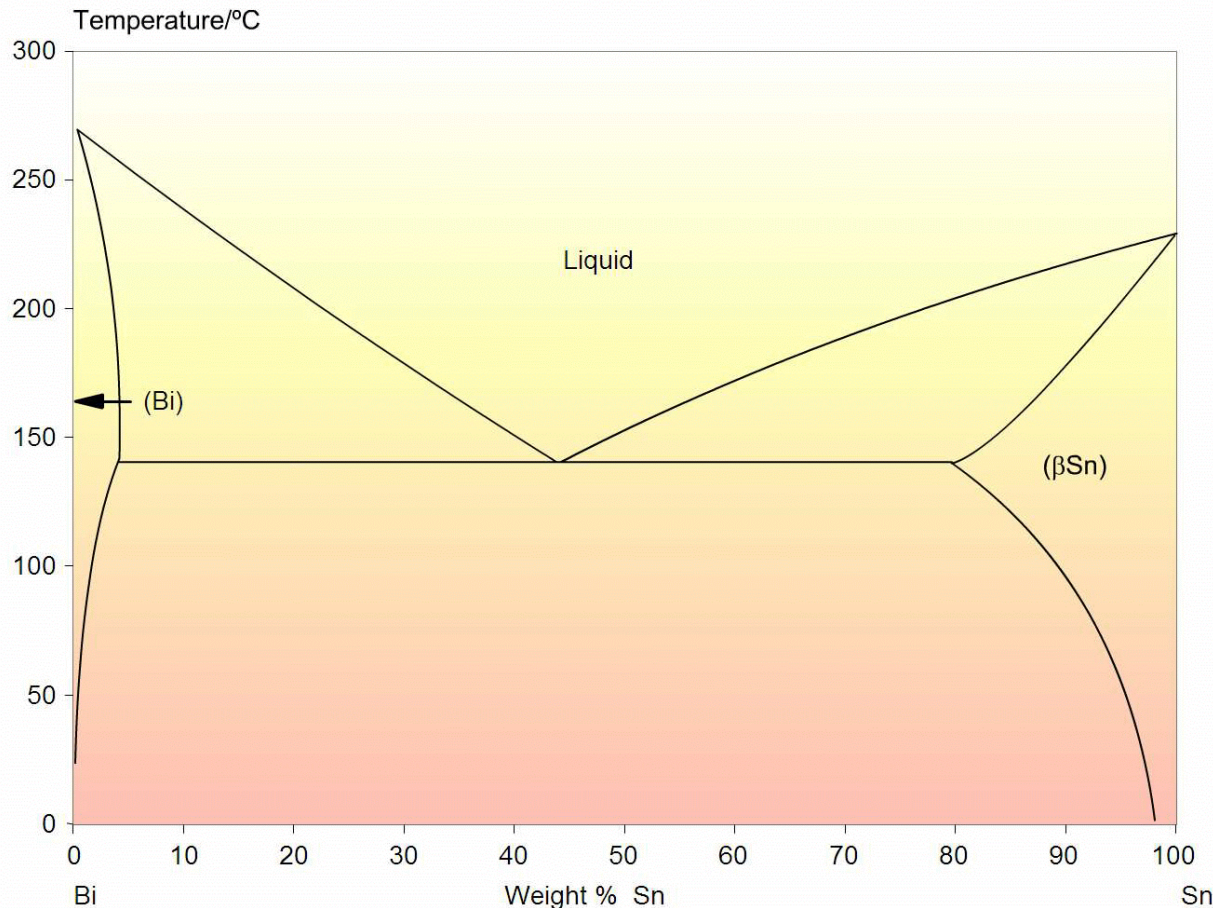


- (1) $a_1 \rightarrow a_2$ Some Na deposited, liquid richer in K
 - (2) $a_2 \rightarrow a_3$ Just below a_3 , solid sample, with solid Na and solid Na_2K
 - (1) $b_1 \rightarrow b_2$ No change until Na begins to deposit at b_2
 - (2) $b_2 \rightarrow b_3$ Solid Na deposits, but reaction happens to make Na_2K (K atoms diffuse into solid Na)
- Here, liquid Na/K in eqb. with Na_2K solid
- (3) $b_3 \rightarrow b_4$ Amount of solid increases until b_4 , liquid hits eutectic point, now a two phase solid is formed

Incongruent melting point: The temperature at which one solid phase transforms into another solid phase plus a liquid phase both of different chemical compositions than the original substance (i.e., the **peritectic temperature**, T_p).

Liquid-Solid Phase Diagrams,

In some binary mixtures, there are regions at high concentrations of either species known as **granular regions**. For instance, in the BiSn binary alloys, there are two regions of interest below.



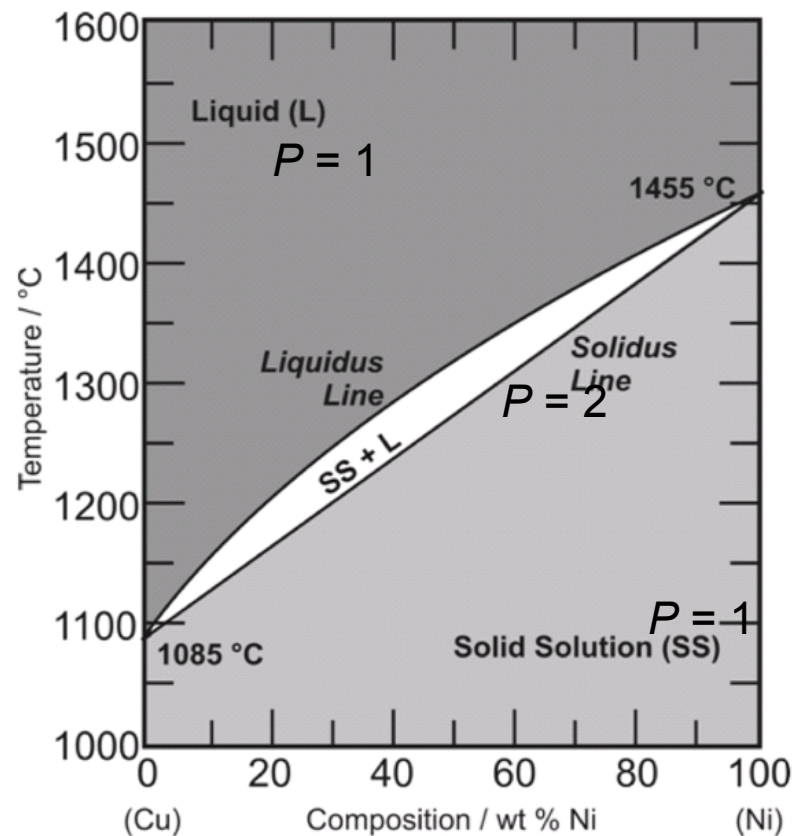
One region, known as β Sn, is basically pure grains of tin doped with small amounts of Bi (i.e., Bi is homogeneously dissolved in Sn).

On the left of the diagram, there is a region of pure Bi, doped with Sn (i.e., Sn is homogeneously doped throughout).

Interactive phase diagram from the website:
http://www.doitpoms.ac.uk/miclib/phase_diagrams.php

Liquid-Solid Phase Diagrams, No Eutectic

In some cases, binary mixtures will not have a eutectic melting point, and the solid-liquid phase diagram will more resemble that of a vapour-liquid diagram. For instance, for a binary mixture of Cu and Ni:



Interactive phase diagram from the website:
http://www.doitpoms.ac.uk/miclib/phase_diagrams.php
See also: <http://www.spaceflight.esa.int>

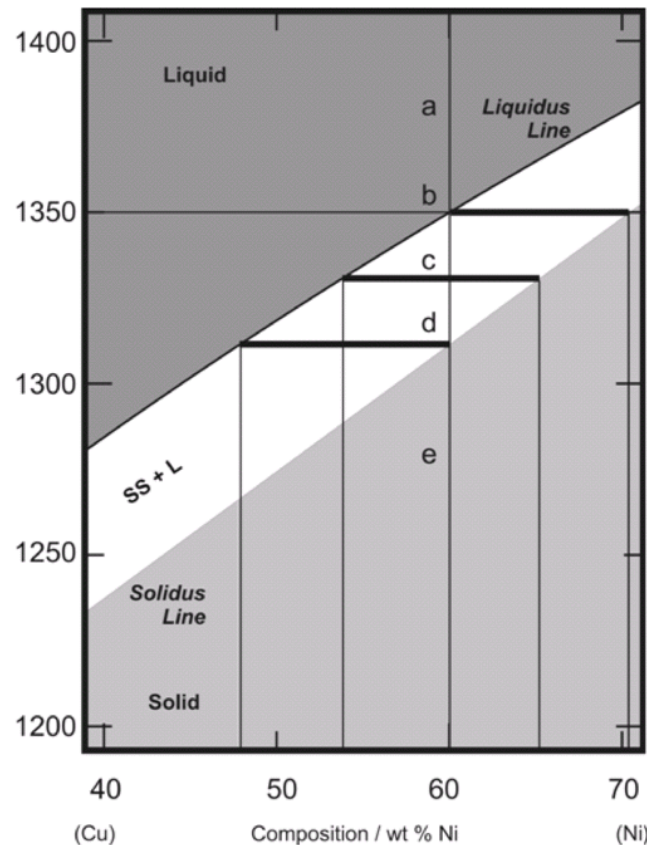
Between the lines, the liquid and solid α -phase of CuNi alloys exist.

Outside of the lines, a single liquid phase exists at high temperatures, and the solid α -CuNi phase exists at low temperatures.

The top line is known as the **liquidus**, which and the bottom line is known as the **solidus**.

Liquid-Solid Phase Diagrams, No Eutectic, 2

Let's zoom in and follow the changes along the isopleth from a - e (as the temperature is dropped):



a. **1375 °C.** The material is above the liquidus line and so the entire mixture is still liquid.

b. **1350 °C.** The first crystals (grains) can start to form. However they are not made of 60% nickel, 40% copper as the only grains that can form are given by the solidus line, which at this temperature has a composition of a little over 70% nickel. As a result of a higher concentration of nickel being drawn from the melt, the liquid becomes enriched with copper.

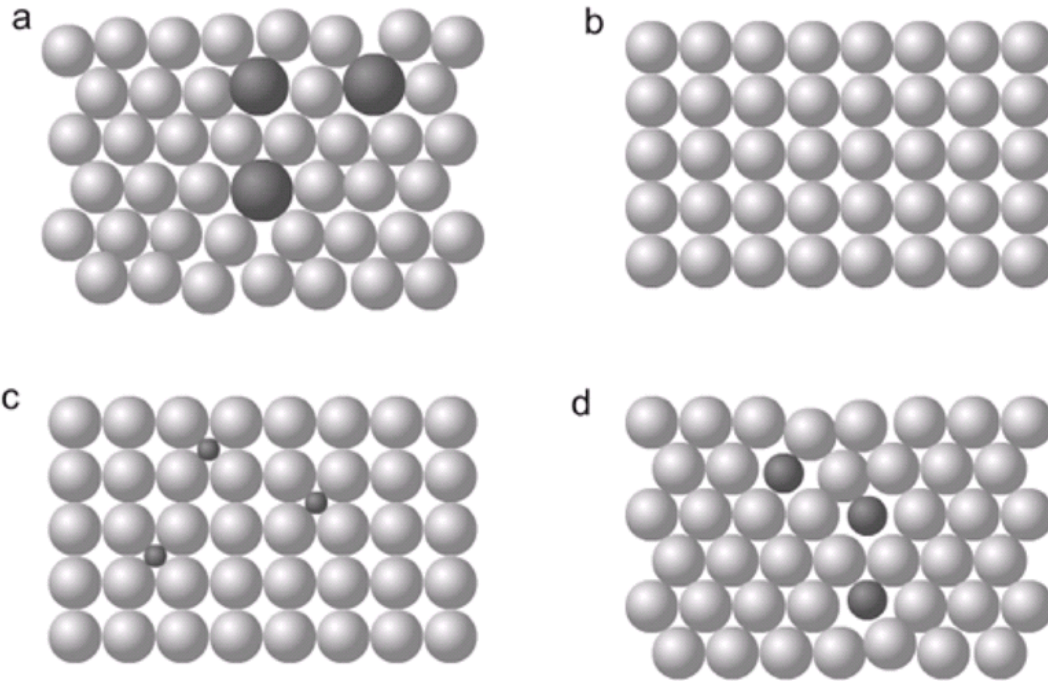
c. **1330 °C.** Mixture is ca. 50:50 solid and liquid. The liquid has a composition of ca. 54% nickel and the surface of the grains is being coated with a solid of 65% nickel. Because the temperature of the grains is only slightly below the melting point (for that particular composition) the individual atoms can still move around to some extent, this is diffusion. As a result the high concentration of nickel in the centre of the grains can diffuse out.

d. **1310 °C.** A tiny amount of liquid is left with a composition of ca. 48% nickel. This solidifies to form the last coating of the grains which end up with a composition of 60% nickel, the same as the original melt.

e. **1280 °C.** The alloy is now fully solid and little diffusion can take place. The grains are uniformly composed of 60% nickel.

Solid Solutions

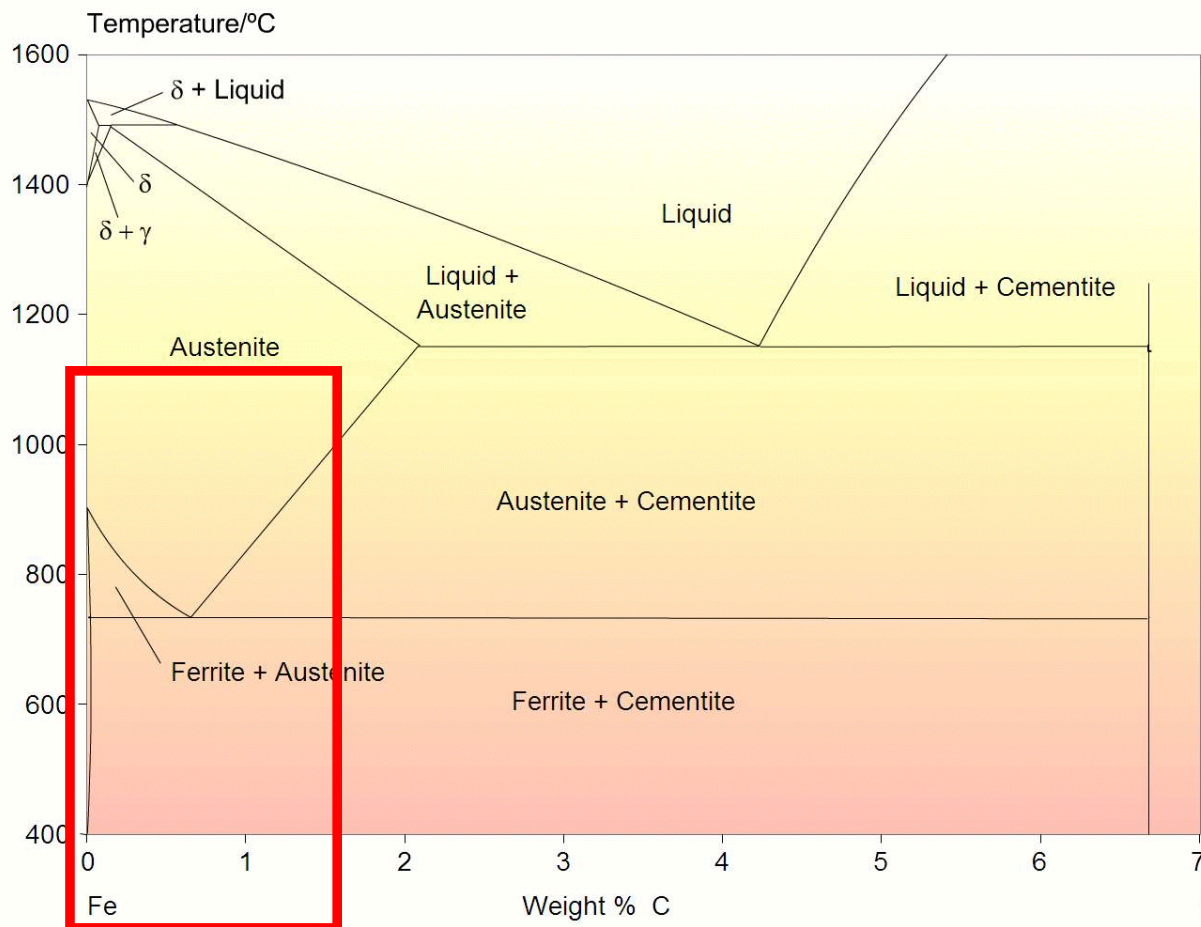
Question: Identify the different 2D diagrams below:



a, d: *substitutional alloys* - small quantities of the dopant replace the more abundant species, do not disrupt the overall crystal structure (Cu,Ni)
c: *interstitial alloy* - small quantities of dopant occupy positions between the abundant atoms (e.g., Fe, C - steel)
b: *pure metal*

Phase Diagram of Steel: FeC

Simple steels are alloys of Fe and C **in the 0 - 1.4% C region**. The α -phase (FCC) is *ferrite* and the γ -phase (BCC) is *austenite*; the latter is less dense than the former due to the packing arrangement of Fe atoms. Fe_3C is known as *cementite*, and *pearlite* is the eutectic mixture of this and α , which is lamellar.



Interactive phase diagram from the website:
http://www.doitpoms.ac.uk/miclib/phase_diagrams.php

- There is a eutectic-like point at **ca. 723 °C** (since austenite is a solid phase in which reactions can take place); hence, this is known as the **eutectoid**.

- The microstructures of steel vary with composition, with hard steels for axles, screwdrivers and chisels around 0.8% C, and brittle steels for razors and knives at ca. 1.4% C.

- The hard steels are lamellar in structure (ca. eutectoid) and the brittle steels at higher %C arise from the presence of cementite and dendrimers.

Getting the Lead out of Bullets

Lead is dense and ductile, has a low melting point, and is inexpensive, making it long prized for molding into ammunition. But it is also **toxic** to birds and other animals that ingest bullets and fragments. To address the need for less toxic ammunition with the same performance as lead bullets, researchers at Oak Ridge National Lab have developed bullets made from a **tungsten-tin composite**



Lead shotgun pellets for waterfowl hunting were banned nationwide in 1991 to prevent poisoning birds. In October, California banned lead ammunition for deer hunting in condor territory. Added restrictions on lead ammo are on the horizon in Missouri as well as other states. **The new bullets are made by compressing a mixture of coarse tin and tungsten powders at about 100,000 psi, under which the tin cold-welds to yield "chunks of tungsten in a sea of tin."**

The composition that best mimics lead is 57% tungsten and 43% tin by weight. Compared with lead-free copper bullets, the tungsten-tin composites are heavier, enabling longer, straighter flight. Used tungsten-tin bullets can be collected from shooting ranges and recycled. The low melting point of tin relative to tungsten means that the bullets can be melted, the tin poured off and repowdered, and the tungsten filtered and reused.

Liquid Crystal Structures: CTAB

Cetyl trimethylammonium bromide (CTAB) is a long-chain **amphiphilic** molecule used in the construction of **lyotropic** liquid crystals (properties dependent upon concentration, and fluidity imparted by the solvent molecules).

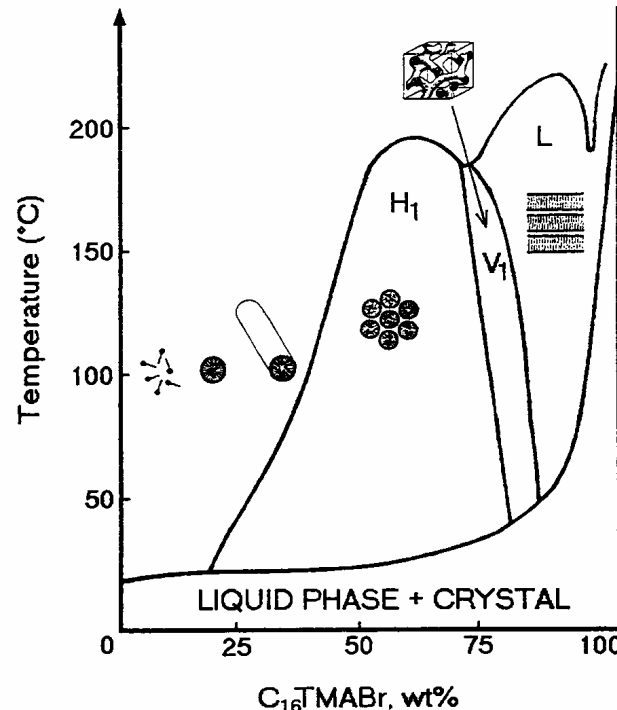
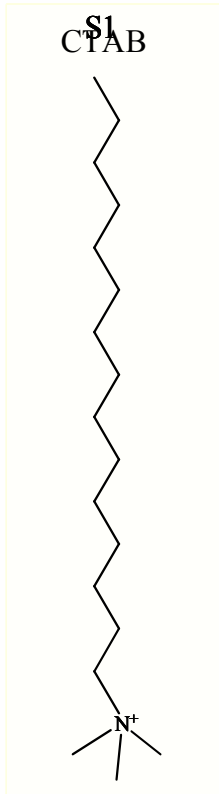


Figure 2. Schematic phase diagram of $C_{16}TMABr$ in water [44].

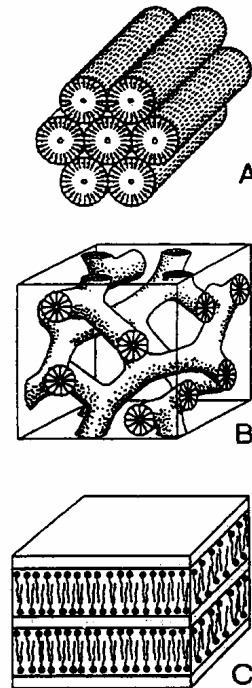


Figure 3. Schematic representation of liquid-crystal structures, (A) hexagonal, (B) bicontinuous cubic, (C) lamellar.

The temp-composition phase diagram of CTAB in H_2O shows the conditions for forming different types of liquid crystal structures, as well as their precursors (micelles and micellar rods).

Final Exam Outline

Material: Exam is comprehensive, but about 60-70% of the focus is upon chapters 6 through 8 (combines all of your general knowledge of thermodynamics)

Question 1:	Mandatory (16 marks)	16
Question 2-9:	Choose seven of eight (12 marks)	84
Bonus Question:	Give this a shot!	4-6 marks

The exam will be marked out of 100, but is worth 45% of your final grade.

How to prepare:

- Nerd notes - summarize each set of notes on one page in an organized form that helps to isolate all key points
- Try the A list problems with your solutions manual
- Attempt the corresponding B list problems
- Review in-class problems
- Download all available handouts, including equation sheets
- Attend tutorials, book consultation times

Physical Chemistry @ U of Windsor

Physical Chemistry (where to go from here?):

- ✓ 59-240: Thermodynamics: Physical & Chemical Properties of Materials
- 59-241: Kinetics, Statistical Thermodynamics & Reactions
- 59-340: Quantum Chemistry - Properties of Molecules
- 59-341: Symmetry & Spectroscopy - Interaction of Light and Matter
- 59-351: Materials Chemistry - Physical Inorganic Chemistry

Honours/Graduate Level

- 59-440: Photochemistry & Kinetics
- 59-441/541: Statistical Mechanics
- 59-445/542: Nuclear Magnetic Resonance (NMR) Spectroscopy
- 59-470/570: Computational Chemistry & Molecular Orbital Theory
- 59-636: Mesomorphic Materials